

ELECTROCHEMICAL STUDIES OF THE RATE OF CHEMICAL REACTIONS  
COUPLED TO CHARGE TRANSFER REACTIONS

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The rates of the reactions of cadmium ion with EDTA species in solutions containing excess calcium ion are being studied using the electrochemical method known as "cyclic voltammetry" or "cyclic stationary electrode polarography" (1). Cadmium ions are introduced into calcium-EDTA solutions by oxidizing a cadmium amalgam by application of a linear voltage scan in the anodic direction. The generated cadmium ions then react with the EDTA species at a rate dependent upon the concentrations of the reactants to form a difficultly and irreversibly reduced complex. Before this complexation reaction is complete, the unreacted cadmium ions may be quickly reduced back into the amalgam by reversing the direction of the voltage scan. The amount of cadmium ion that reacts with the EDTA species is determined by comparing the cathodic faradaic current with the anodic current. The rate of the repetitive anodic and cathodic scans (cycles/sec) establishes a time base for the experiment and makes it possible to calculate pseudo first-order rate constants from the electrochemical data. The rate processes being studied have half-lives in the range of 10 to 1000 milliseconds.

In order to calculate second-order rate constants from the electrochemically determined pseudo first-order rate constants, it is necessary to consider the equilibrium process in solution. Procedures were devised to determine the formation constants and to calculate the activities of all the EDTA species present in solution under the conditions of the experiment. These methods are similar to the methods originally developed by Schwarzenbach (2) in basic approach, but are more precise due to computerized methods of data processing now available. Equations are derived for the acid-base titration curves of the parent acid EDTA in the presence of excess calcium ion and potassium nitrate. Simultaneous equations are then solved by the computer using the data from the pH titration curve to calculate the various equilibrium constants. Previously unreported species were detected and their formation constants determined.

The overall problem can be divided into two parts: (1) The electrochemical measurement of the pseudo first-order rate constants. (This involves development of the technique and methodology and the design and construction of the electronic equipment and electrochemical cells.) (2) The potentiometric measurement of the equilibrium constants needed to compute the appropriate second-order rate constants from the electrochemically measured pseudo first-order rate constants. These two parts of the problem will be discussed separately.

The Electrochemical Experiment

The diffusion equations applicable to a reversible electrochemical reaction in which the product of that reaction is deactivated by a further irreversible reaction with a substance in solution have been derived for many of the electrochemical techniques. The theoretical treatment of this type of system for the cyclic stationary-electrode polarographic method has been published by Shain and co-workers. (1)

In the present work, the experiment does not correspond exactly to the model Shain used in his theoretical treatment. The electroactive species is

present initially in its reduced form so that the first scan is anodic and performs an oxidation rather than a reduction as described by Shain. During the initial anodic scan, the cadmium amalgam is oxidized into a calcium-EDTA solution and the cadmium ion so produced undergoes a spontaneous reaction with the EDTA species to form a species which is not electroactive at the potential of reduction of hydrated cadmium ion. During the reverse cathodic scan the uncomplexed cadmium ion is reduced back into the amalgam. Thus, the ratio of cathodic to anodic peak currents rather than the ratio of anodic to cathodic peak currents is related to the rate constant.

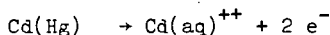
The electrochemical cell used in this work incorporates a strictly planar mercury electrode (4) with a Luggin capillary probe as shown in Figure 1.

Cadmium amalgam is prepared by reducing cadmium nitrate solution at constant potential into mercury. The transfer of the amalgam to the cell must be performed in a closed system under a nitrogen atmosphere to avoid rapid air oxidation of the cadmium from the amalgam.

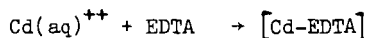
The three-electrode, potentiostatic circuit used to apply the cyclic potential program to the working electrode is a conventional operational amplifier circuit. The complete electronic configuration is shown in Figure 2.

The cyclic scan generator (3) is also an operational amplifier instrument which is capable of supplying continuously variable cycling rates ranging from 100 sec/cycle to 100 cycle/sec.

If  $1 \times 10^{-4} M$  cadmium amalgam is oxidized and then reduced as described above in contact with a solution buffered at pH 8 and containing 0.01 M EDTA and 1.0 M  $KNO_3$ , with no calcium ion present, an anodic current is observed that corresponds to the reaction:



No cathodic current is observed under these conditions on the subsequent reduction cycle, even though the cycling rate is increased to as much as 100 cycles/sec. This means that, even during the very short time corresponding to the experiment carried out at 100 cycles/sec, the reaction



has gone essentially to completion. Since 100 cycles/sec is the upper limit of the cycling rate allowed by the electronics and also by the reversibility of the  $Cd^{++}/Cd(Hg)$  couple, it is necessary to slow down the coupled chemical reaction in some way in order to apply the cyclic voltammetric method to its study. The reaction can be slowed down by reducing the concentration of the reactant EDTA species to a lower level. A convenient way to achieve this is to add an excess of some metal ion to the solution which forms labile complexes with the EDTA and yet is inactive at the potential of the  $Cd/Cd^{++}$  couple. For example, addition of excess calcium ion to the solution buffers the solution with respect to the free EDTA species at a very low concentration determined by the equilibrium constants of the system. As long as the rates of the dissociation and recombination reactions of the  $Ca^{++}$ -EDTA system are much faster than the rates of the reactions between the free EDTA species and cadmium ion and, as long as the free calcium ions and the calcium-EDTA complex ions are in large excess of the reacting cadmium ions at all times, the concentrations of the free EDTA species will remain essentially constant and will not be affected by their reaction with cadmium ion.

The following table shows some data obtained with this system.

Table I

Electrochemical Data for Determination of Pseudo First-order Rate Constants.  
 Solution Conditions:  $\Sigma_{Ca^{++}} = 0.0159 \text{ M}$ ;  $\Sigma_{EDTA} = 0.0120 \text{ M}$ ;  $\text{pH} = 9.210$  (0.05 M Boric acid - NaOH Buffer);  $\mu = 1.0 \text{ M}$  ( $\text{KNO}_3$ );  $T = 25.0^\circ\text{C}$ .

Current Ratio	$\tau$ (sec.)	$k\tau$	$k$ ( $\text{sec}^{-1}$ )	$k\tau$ "calculated"
0.473	0.3585	1.125	3.14	1.133
0.711	0.1215	0.375	3.09	0.384
0.772	0.0879	0.272	3.09	0.278
0.806	0.0699	0.224	3.20	0.221
0.729	0.1062	0.343	3.23	0.336
0.650	0.1639	0.505	3.08	0.518
0.523	0.2750	0.900	3.27	0.869

AVE = 3.16

Because of the rather fast cycling rates, it was necessary to display the current-voltage curves on an oscilloscope and to photograph the oscilloscope screen. The resulting photographs were analyzed using methods described by Nicholson (3). The experimental results are shown in the first two columns of Table I. The values of  $k\tau$  entered in the third column of the table were obtained by extrapolation from the theoretical curve of  $(i_{cp}/i_{ap})$  vs.  $k\tau$  as described by Shain (1). The values of  $k$  were obtained by dividing the appropriate values of  $k\tau$  by the experimental values of  $\tau$ . The "calculated" values of  $k\tau$  were obtained by multiplying the average value of  $k$  by each experimental value of  $\tau$ . When these "calculated" values of  $k\tau$  are plotted vs. the experimental current ratios, the solid points in Figure 3 are obtained. The solid curve in this figure is the theoretical line calculated by Shain. The diagram demonstrates that the experimental data do indeed correspond to the coupled reaction model used to solve the diffusion equations. Meaningful pseudo first-order rate constants can therefore be obtained and, if the concentrations of various EDTA and EDTA-complex species are calculated, the dependence of the rate of the reaction on these species can be determined.

#### Measurement of Equilibrium Constants

If a solution containing tetraprotic EDTA,  $\text{H}_4\text{Y}$ , and an excess of inert supporting electrolyte added to control the ionic strength is titrated with strong base, the titration curve can be used to evaluate the successive acid dissociation constants of the free acid. If  $\text{H}_4\text{Y}$  is also titrated in the presence of a slight excess of calcium ion, the data from this titration curve can be combined with the  $K$ 's for the free acid to allow calculation of the formation constants of all the calcium-EDTA species formed. In order to make the calculations as general as possible, provision was made for the possible existence of two protonated Ca-EDTA complexes.

All calculations were computerized in order to minimize the time spent in calculation, to make it possible to use more data points and to obtain increased precision by averaging the results. The computer programs are written in Fortran and were used with a Control Data Corporation 3600 Computer at the Research Computing Center of Indiana University. The programs utilize the basic data from the experiment (initial M moles of  $\text{H}_4\text{Y}$ , ml of base corresponding to an equivalent of acid, initial volume, pH, ml of base added, and mmoles of  $\text{Ca}^{++}$  present) and solve the appropriate simultaneous equations using the method of determinants. Some typical experiments and results are shown in Table II.

Table II

Potentiometric Determinations of Formation Constants for Ca-EDTA System.

Experiment	Number of Simultaneous Eq'ns Solved	Average Value of K
Titration of $1 \times 10^{-3}M$ $H_4Y$ - $1.0 M KNO_3$ From $a = 0$ To $a = 2$ With $KOH$ - $1.0 M KNO_3$ ; $T = 25.0^\circ C$	13 Equations Solved From 26 Data Points	$K_1 = 6.15 \times 10^{-3}$ $K_2 = 2.41 \times 10^{-3}$
Titration of $1 \times 10^{-3}M$ $H_4Y$ - $1.0 M KNO_3$ From $a = 3$ to $a = 4$ with $KOH$ - $1.0 M KNO_3$ ; $T = 25.0^\circ C$	24 Equations Solved From 48 Data Points	$K_4 = 1.36 \times 10^{-10}$ $K_{KY} = 0.37$
Titration of $1 \times 10^{-3}M$ $H_4Y$ - $3 \times 10^{-3}M Ca^{++}$ - $1.0M KNO_3$ From $a = 0$ to $a = 4$ with $KOH$ - $1.0M KNO_3$ ; $T = 25.0^\circ C$	12 Equations Solved From 36 Data Points	$K_{CaY} = 4.33 \times 10^{+9}$ $K_{CaHY} = 1.94 \times 10^{+3}$ $K_{CaH_2Y} = 27.4$

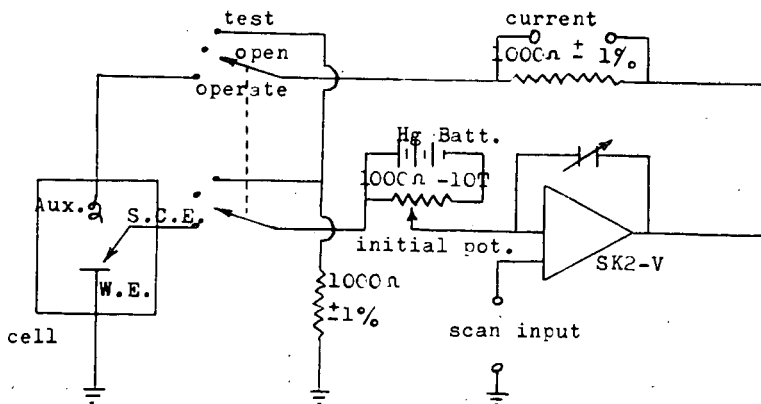
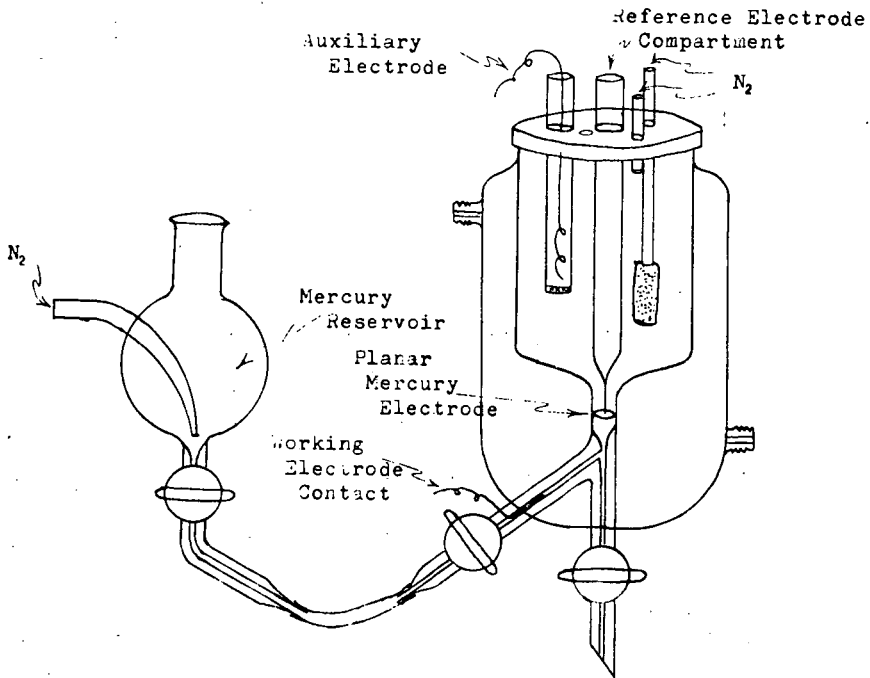
Equilibrium constants obtained in this manner can be used to calculate the concentrations of EDTA species present at any pH in potassium nitrate solutions of ionic strength 1.0. Two plots giving the fraction of each EDTA species present in solution as a function of pH in the absence and in the presence of excess calcium ion are shown in Figures 4 and 5. The species  $KY^{-3}$ ,  $CaHY^{-}$  and  $CaH_2Y$ , whose formation constants have not been previously reported, were found to be present at appreciable concentrations.

#### References

- (1) Nicholson and Shain, Anal. Chem., **36**, 706 (1964).
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- (3) DiSalvo and Schaap, to be published.
- (4) Kuempel and Schaap, Anal. Chem., **38**, 664 (1966).
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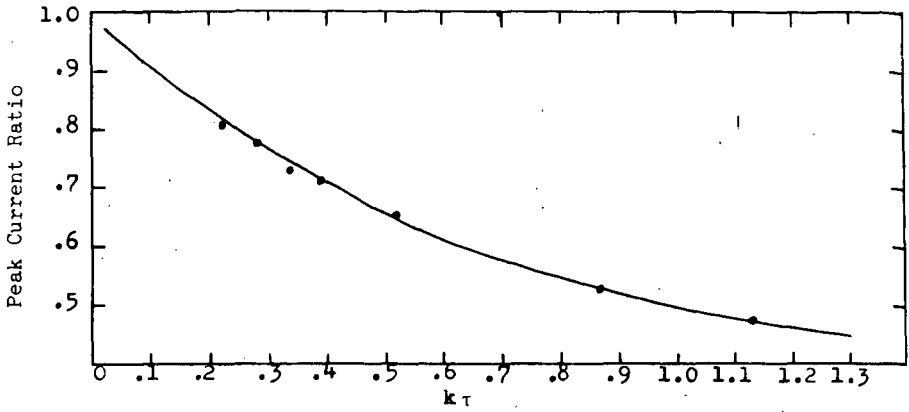


Figure 3: Experimental and Theoretical Plot of  $k\tau$  vs Peak Current Ratio

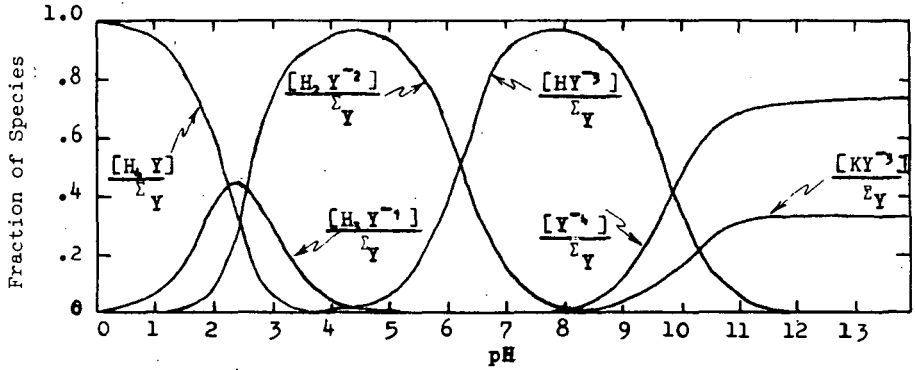


Figure 4: pH vs Fraction of Species plot for EDTA  
 $\mu = 1.0$  ( $KNO_3$ );  $T = 25.0^\circ C$

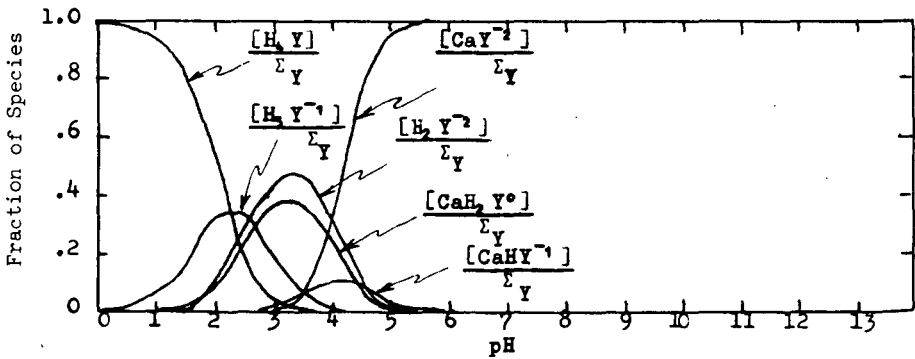


Figure 5: pH vs Fraction of Species Plot for Ca-EDTA  
 $\mu = 1.0$  ( $KNO_3$ );  $T = 25.0^\circ C$ ;  $\Sigma Ca^{++}/\Sigma EDTA = 2.0$